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OPTICAL ABSORPTION OF TNT SINGLE
CRYSTALS

David S. Downs, et al

Picatinny Arsenal
Dover, New Jersey

August 1973

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Technical Report 4585

**OPTICAL ABSORPTION OF TNT
SINGLE CRYSTALS**

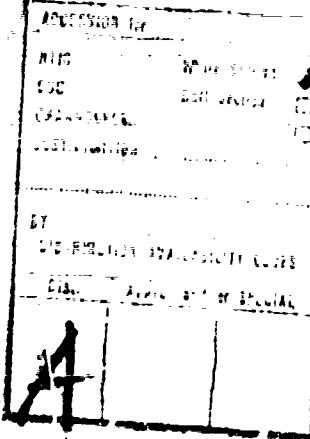
by
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ABSTRACT

A method for growing large area, thin, single crystal platelets of TNT is reported. The optical absorption properties of these crystals was studied, and dichroic behavior was observed. The absorption edge is approximately 3.1 eV and is tentatively assigned to $n(\text{NO}_2) \rightarrow \pi^*$ transitions by comparison with solution spectra.

INTRODUCTION

Knowledge of the fundamental optical and electronic properties of reactive materials has been shown to be of crucial importance to the understanding of the characteristic phenomena in these materials. Previously, the optical absorption spectrum of TNT has been obtained in solutions^{1,2,3}, but to our knowledge not in thin film or single crystal form. Techniques for growing large single crystals of TNT from the melt or from saturated solution are well known. However, the purity of samples prepared by these techniques is questionable because of solvent occlusions; and they are difficult to cut and polish for optical measurements.

We have succeeded in growing large area, thin, single crystal platelets of TNT suitable for both optical and electronic measurements, and report here the method of growth and optical absorption properties of these crystals.

EXPERIMENTAL

A. Crystal Preparation

Crystal growth from the vapor phase, following one or more purifications, works very well with substances having appreciable vapor pressures below their melting points. This technique is always worth consideration if the substance dissociates or decomposes on or before

melting. The important variables in this technique are the temperature of the vaporizing substance and that of the collector surface. Entrainer sublimation using high purity inert gases, Argon for example, tends to speed up the process and encourage the growth of crystals of larger surface area, since the carrier gas assists in the removal of heat of sublimation.

A commercially available vacuum sublimator (Kontes Model K-855600) was used for the crystal preparation. Approximately 2 gms of TNT (Eastman Kodak), purified by the VanDolah process⁴, was placed in the vessel for each sublimation. The vessel was partially immersed into a controlled temperature bath as shown in Figure 1. A teflon collar was fitted on the finger to minimize the amount of material deposited on the upper surfaces of the vessel. Silicone oil in the inner finger helped to maintain a constant finger temperature. It was not found necessary to control the finger temperature separately to crystallize TNT.

After evacuating the vessel to forepump pressure, with a liquid nitrogen trap in the foreline, the system was flushed at least twice with an inert gas and then backfilled to the desired pressure and sealed off before immersion in the bath. Since TNT melts at about 80°C, the temperature was maintained at 70°C. At this temperature the vapor pressure of TNT is approximately 5×10^{-4} Torr⁵. Also, the rate of thermal decomposition at this temperature is relatively low. (With

materials of this type a compromise has to be made between a temperature which provides a suitable vapor pressure and one which produces a very slow rate of thermal decomposition.)

Small chunky TNT crystals with well defined faces were produced when Helium was used as the ambient gas. However, our objective was to grow thin single crystal platelets, and the most suitable condition for this growth habit was found to be 25 cm of Argon which produces a finger temperature of approximately 55°C at the 70°C bath temperature. Typical platelets are shown in Figure 2. These crystals, when viewed under a polarizing microscope, prove to be single crystals and essentially strain free. Typical thicknesses are on the order of 10 μ - 40 μ .

It should be stressed that the growth conditions are rather critical and changing the geometry can drastically affect the temperature gradient and subsequently the growth habit.

B. Absorption Studies

Optical density measurements were obtained at room temperature and 77°K using a Cary 14R spectrophotometer. In order to investigate the absorption of polarized light at room temperature, a rotating sample holder was designed. Figure 3 shows the sample holder with the circular mask on which the crystal is mounted. A u.v. polarizer (Polaroid Type HNP'B) was placed in the beam and the sample rotated about an axis parallel to the beam thus eliminating effects of partial polarization from the light source and nonuniform beam intensity. Partial absorption due to the polarizing sheet was subtracted from the crystal spectrum.

RESULTS

X-ray studies of the sublimed platelets of TNT showed that they have orthorhombic symmetry with $a=15.0$, $b=20.0$, $c=6.05$. The ac -plane lies in the plane of the platelet with the c -axis parallel to the elongated direction of the plate. This situation is depicted in Figure 4.

The typical optical absorption spectrum of a TNT crystal is shown in Figure 5. There is essentially no absorption through the visible region of the spectrum with the onset of strong absorption occurring at approximately 400 nm (3.1 eV) for unpolarized light. Spectra have also been obtained at 77°K and essentially no shift in the position of the absorption edge was observed. Most of the samples investigated exhibit interference effects in the visible region of the spectrum.

Optical absorption as a function of the angle between the plane of polarization and the crystalline c -axis is shown in Figure 6. The absorption coefficient is larger for light polarized perpendicular to the c -axis ($E \perp c$), and increases by a factor of about 1.7 over that for $\vec{E} \parallel c$ in the region of strong absorption. The absorption edge for \vec{E} parallel and perpendicular to the c -axis is shown in Figure 7.

DISCUSSION

The correlation between the crystallographic data and the refractive indices of orthorhombic TNT was made by Rauch and Coleman⁶ as shown in Table I.

<u>Unit Cell Dimension (A)</u>	<u>Refractive Index⁷ (5893Å)</u>
a = 15.0	$n_a(\gamma) = 1.717$
b = 40.0 (20.0)	$n_b(\alpha) = 1.545$
c = 6.05	$n_c(\beta) = 1.674$

They determined that some of their sublimed single crystals were monoclinic with $\beta = 111^\circ 15'$ ($\beta \equiv$ angle between a and c axes), however, a pseudo orthorhombic symmetry was also observed with $\beta = 90^\circ 30'$. In all, at least seven morphological types of TNT have been identified. However, it has been noted that, although TNT crystals grown by the usual laboratory methods exhibit a variety of types from the same crystallizing medium, the sublimation method consistently produces crystals of a single type⁸. It is anticipated that crystals grown by the technique described above will be useful for structure determination.

Molecular orbital calculations were used by Rauch and Coleman to predict the absorption spectrum of TNT⁹. Based on a planar configuration with all atoms in the plane except for the hydrogens of the methyl group, a strong ($\pi \rightarrow \pi^*$) transition is predicted at 255 nm which the

authors correlated with the 227 nm band observed in the solution spectrum. In addition, weaker $n(\text{NO}_2) \rightarrow \pi^*$ transitions were predicted at longer wavelengths which are also observed in solution spectra. In fact, by comparing the spectra of several polynitrobenzenes and TNT in various solvents, the band at 340 nm has been shown to be related to the nitro group. The solution spectrum of TNT in ethanol is shown in Figure 8, along with a spectrum obtained on one of our thinnest TNT samples. (Note that the solution absorption is plotted on a logarithmic scale.)

In general, it is found that the spectrum of the molecular crystal differs from the spectrum of the free molecule in the following respects:

- a) A general displacement of the spectrum arising from the difference in Van der Waal's (and other) interactions between an excited molecule and the crystal on the one hand and with vacuum or solvent on the other.
- b) There is a complete or partial removal of the degeneracy of the molecular state because of the crystal field.
- c) There is an increase in the number of transitions in the crystal because of the transformation properties imposed on the stationary crystal states by the symmetry of the crystal.
- d) Because of the symmetry of the molecular site in the crystal, transitions which are forbidden in the free molecule become formally allowed in the crystal¹⁰.

The similarity between the low energy regions of absorption in the solution and crystal spectra leads one to suspect that if the theory is correct in predicting $n(\text{NO}_2) + \pi^*$ transitions as the low energy transitions in the TNT molecule then these may also be the transitions responsible for the low energy absorption in the crystal.

The dichroism observed in the polarized absorption spectra indicates that the transitions involved in the low energy absorption are polarized more strongly along the a-axis of the crystal. This is consistent with the relative optical dielectric constants which are 2.95 and 2.78 along the a and c-axes, respectively. Unfortunately, the molecular arrangement of the unit cell is not known and therefore we cannot correlate these results with the configuration of the molecule.

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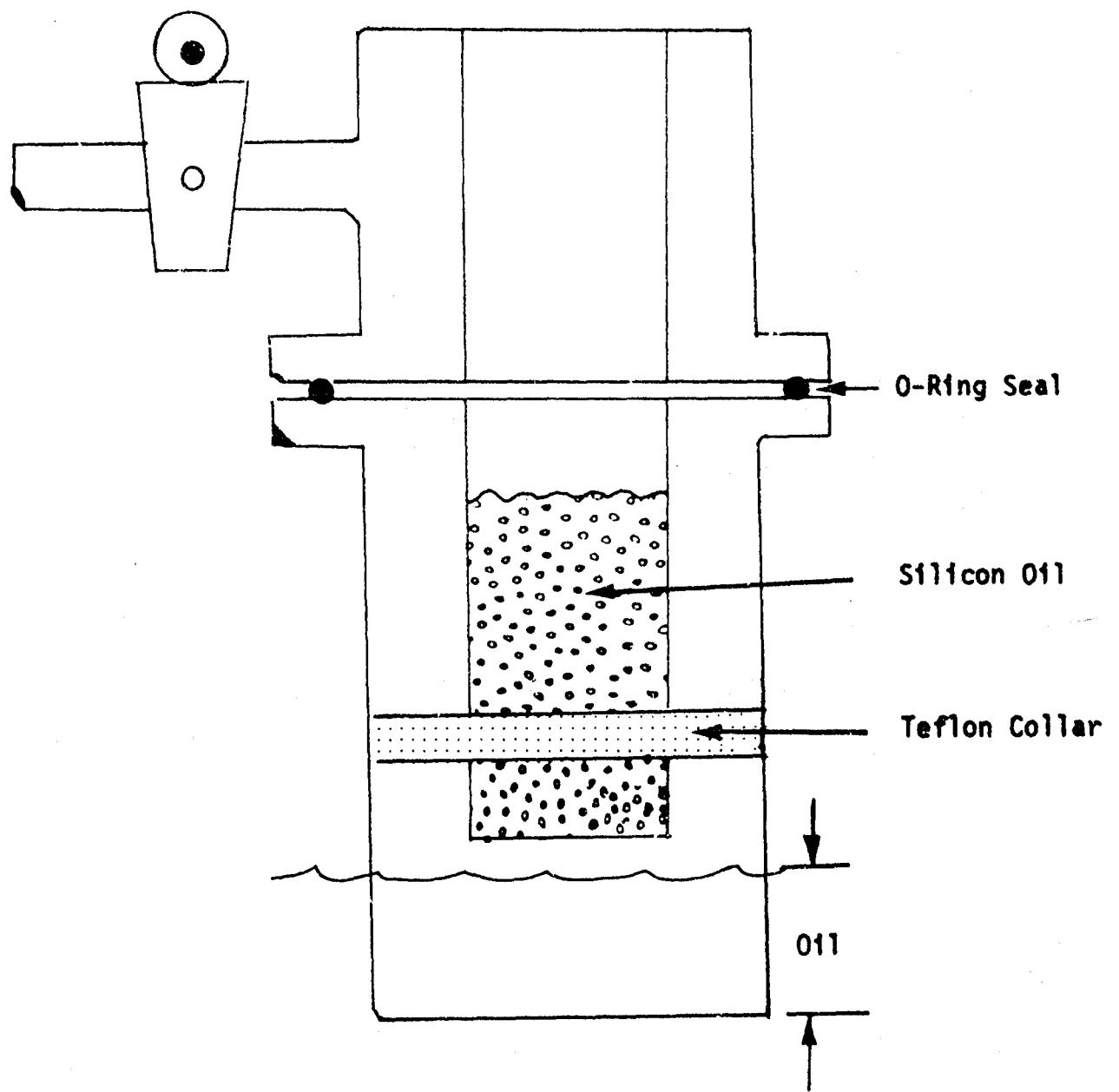


FIGURE 1 Schematic of the Sublimation Apparatus

FIGURE 1. Typical soil physical characteristics of the surface soils of the tropical savanna.

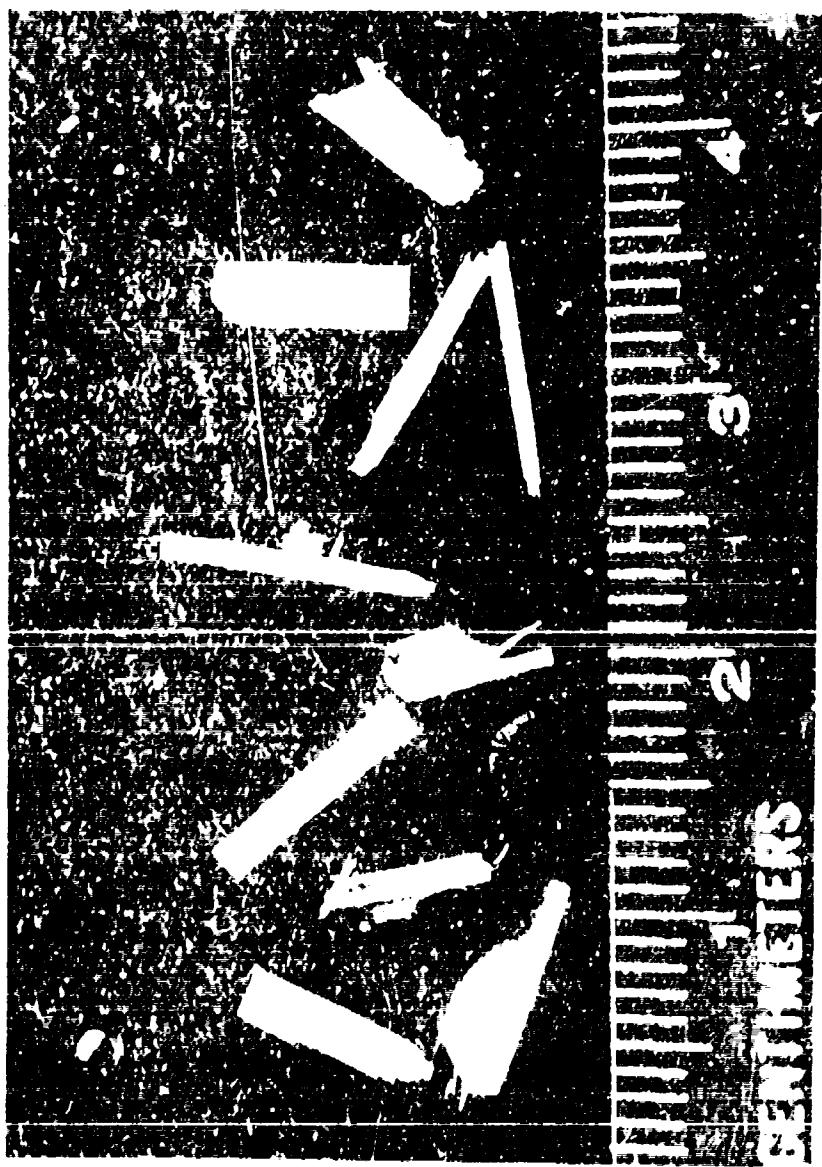
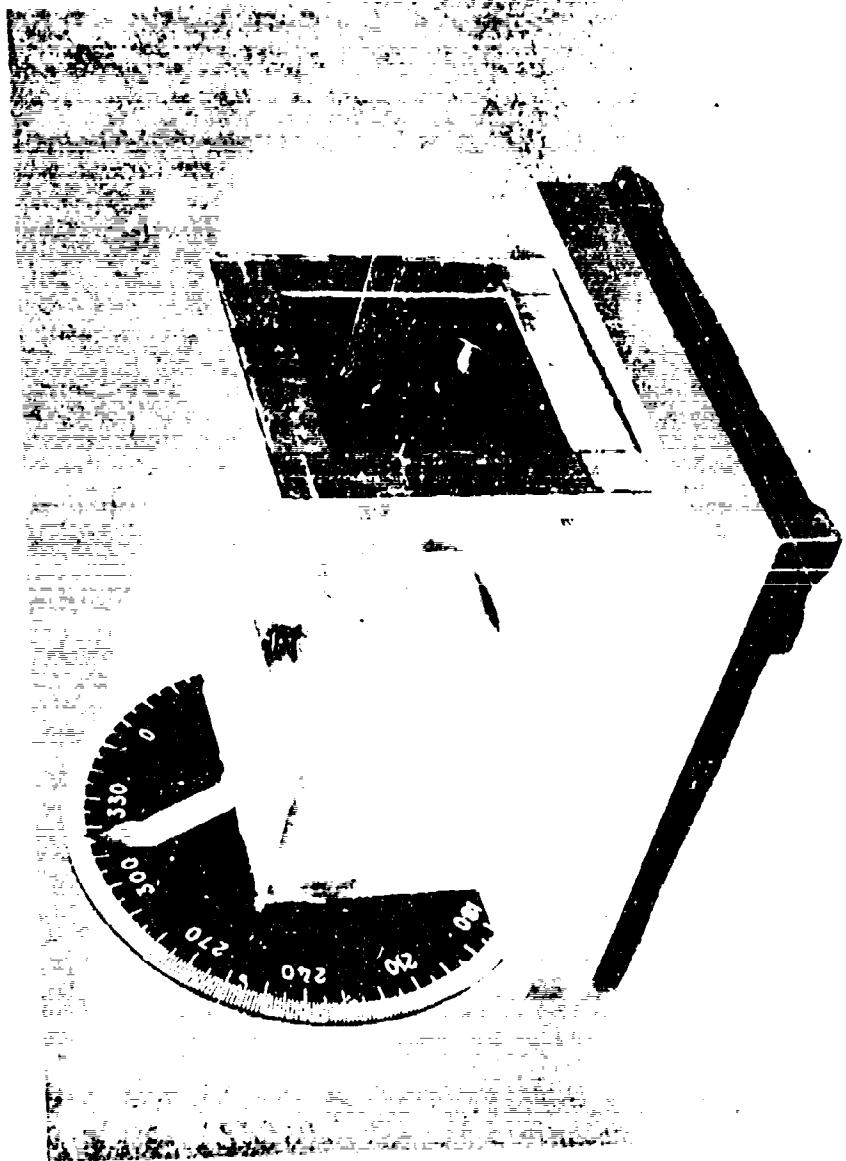


Figure 5. Circular scale used to judge the degree of secondary



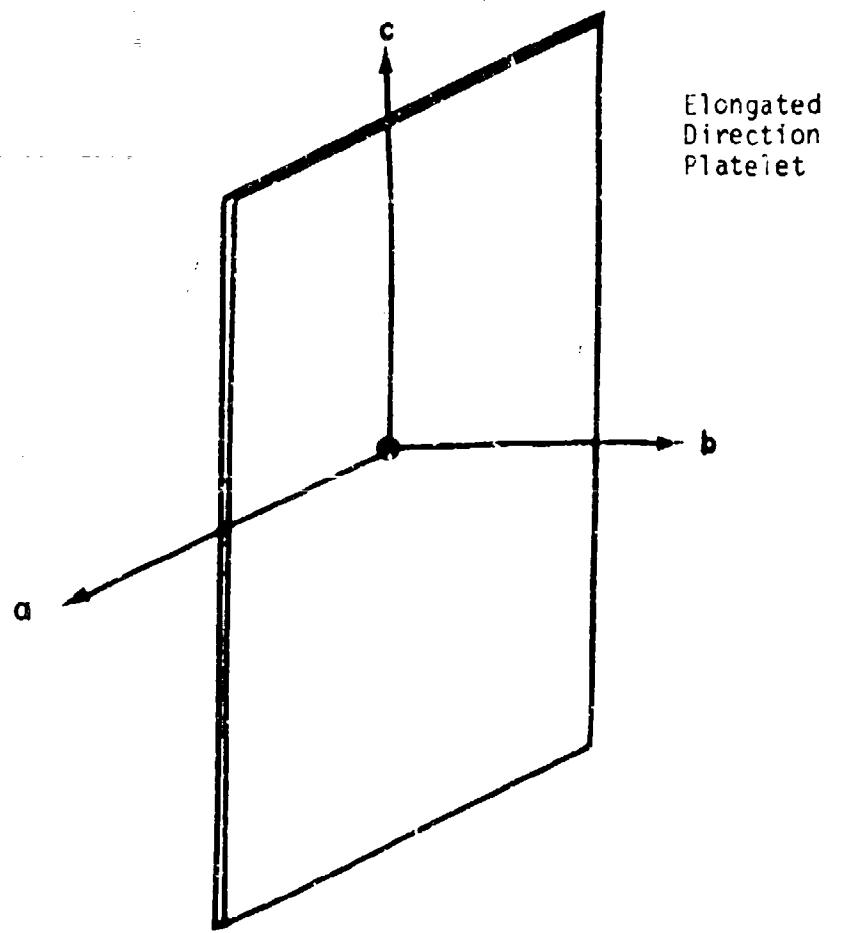


FIGURE 4 Relationship between crystal morphology and axes of the unit cell for sublimed platelets.

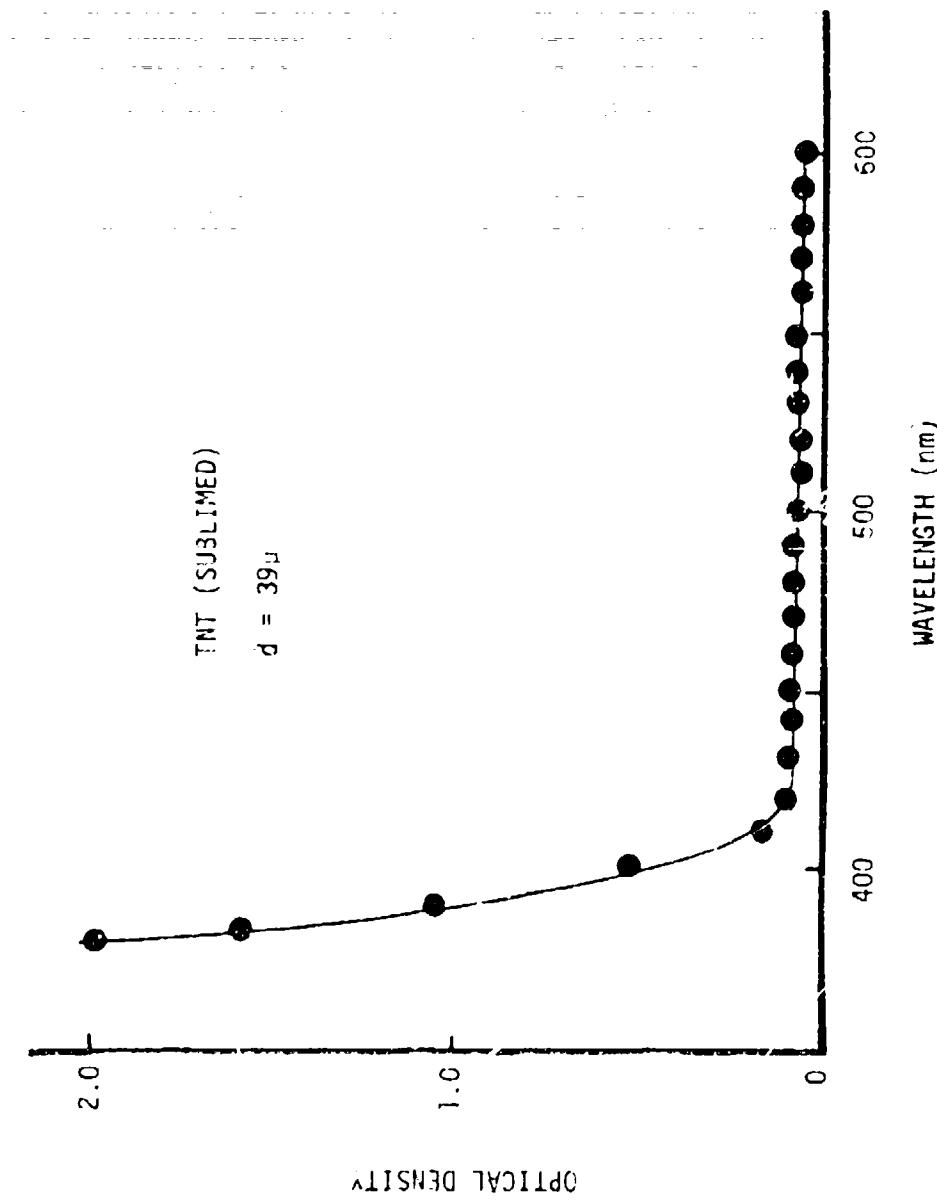


FIGURE 5 Typical Room Temperature Absorption Spectrum

$$\alpha = 2.3 \frac{O.D.}{I} = 2.3 \times \frac{1.0}{10^{-3} \text{ cm}} = 2.3 \times 10^3$$

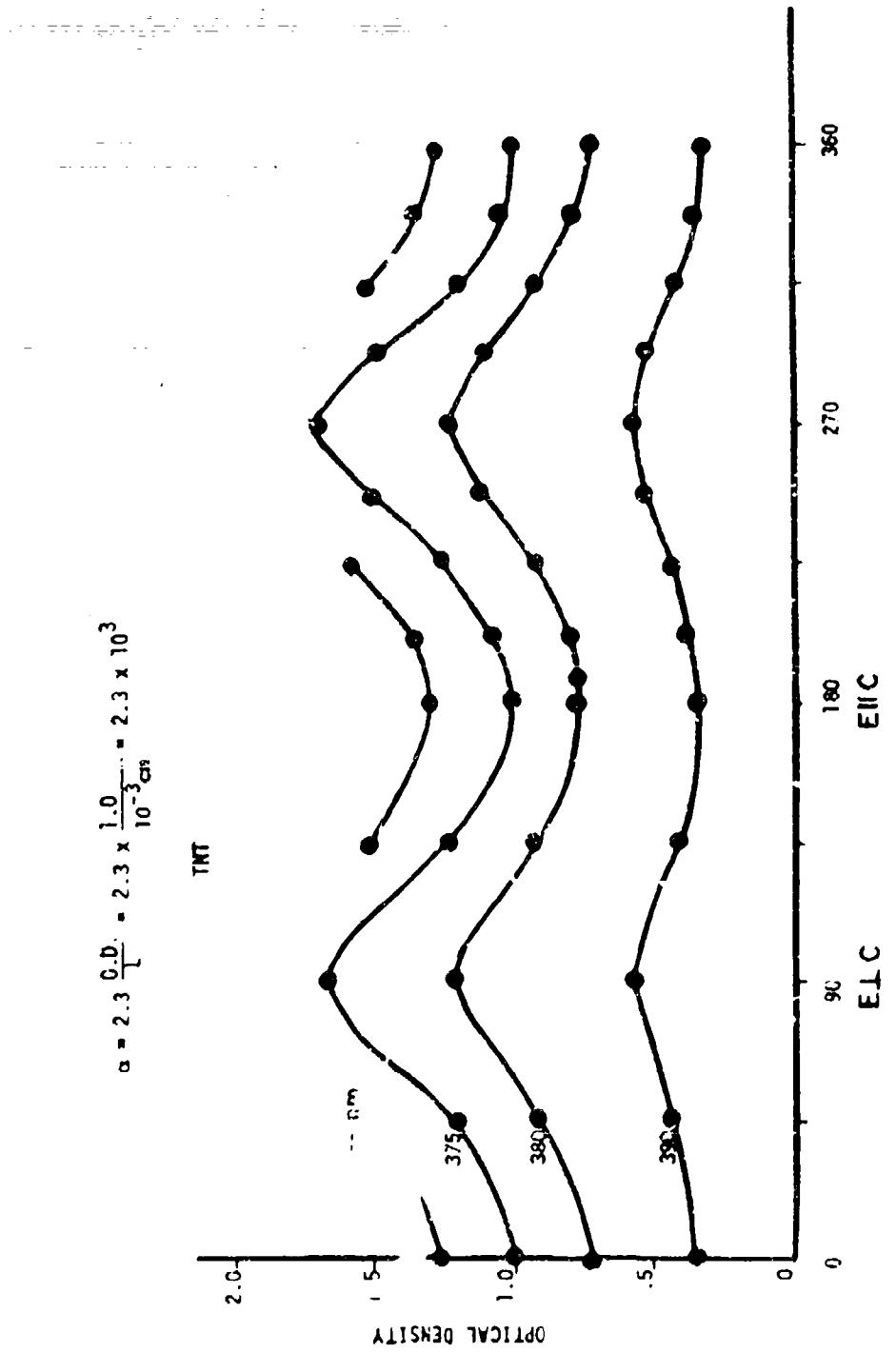


FIGURE 6 Absorption as a function of angle between the c-axis and the plane of polarization.

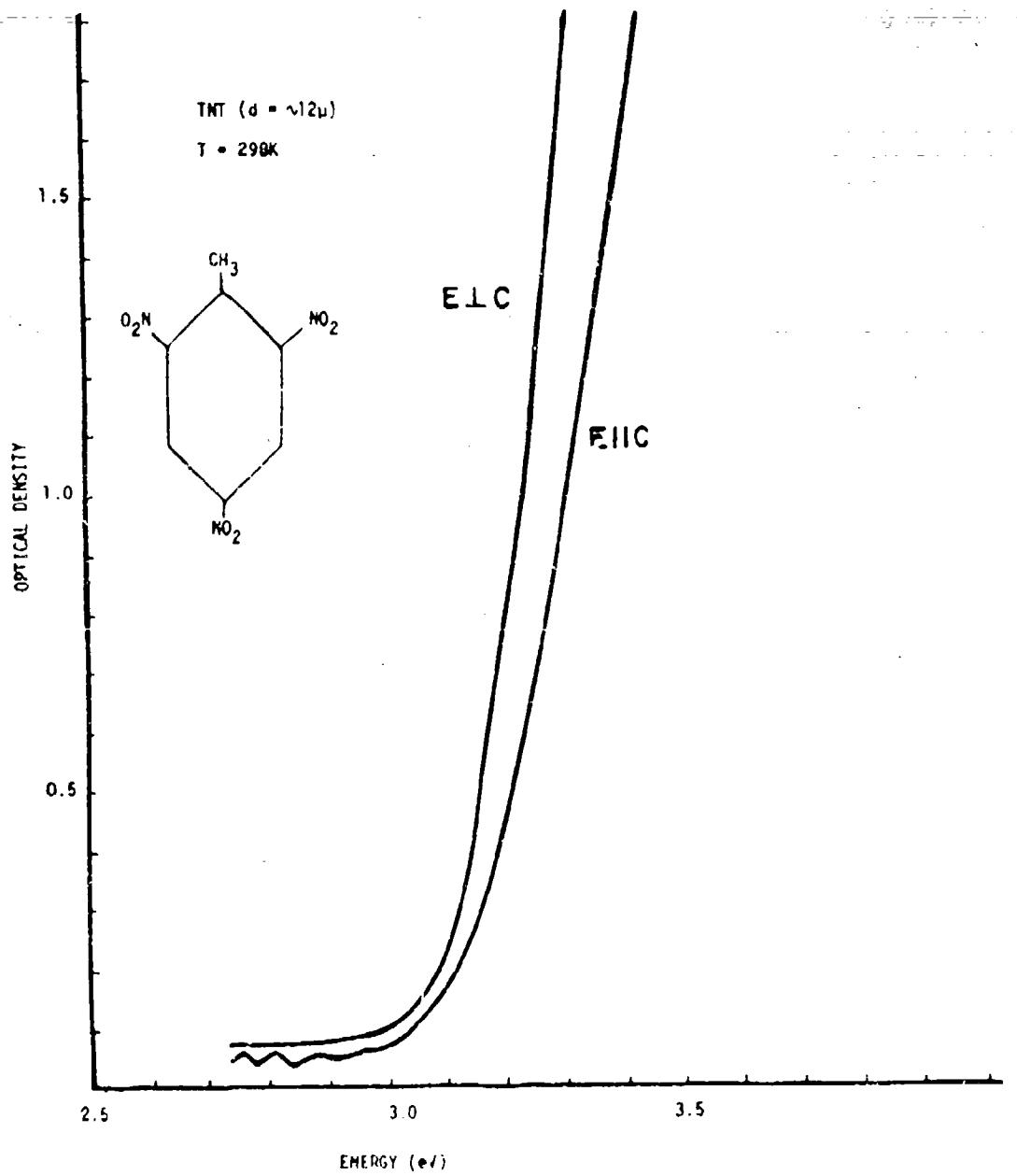


FIGURE 7 Room temperature absorption with polarized light.

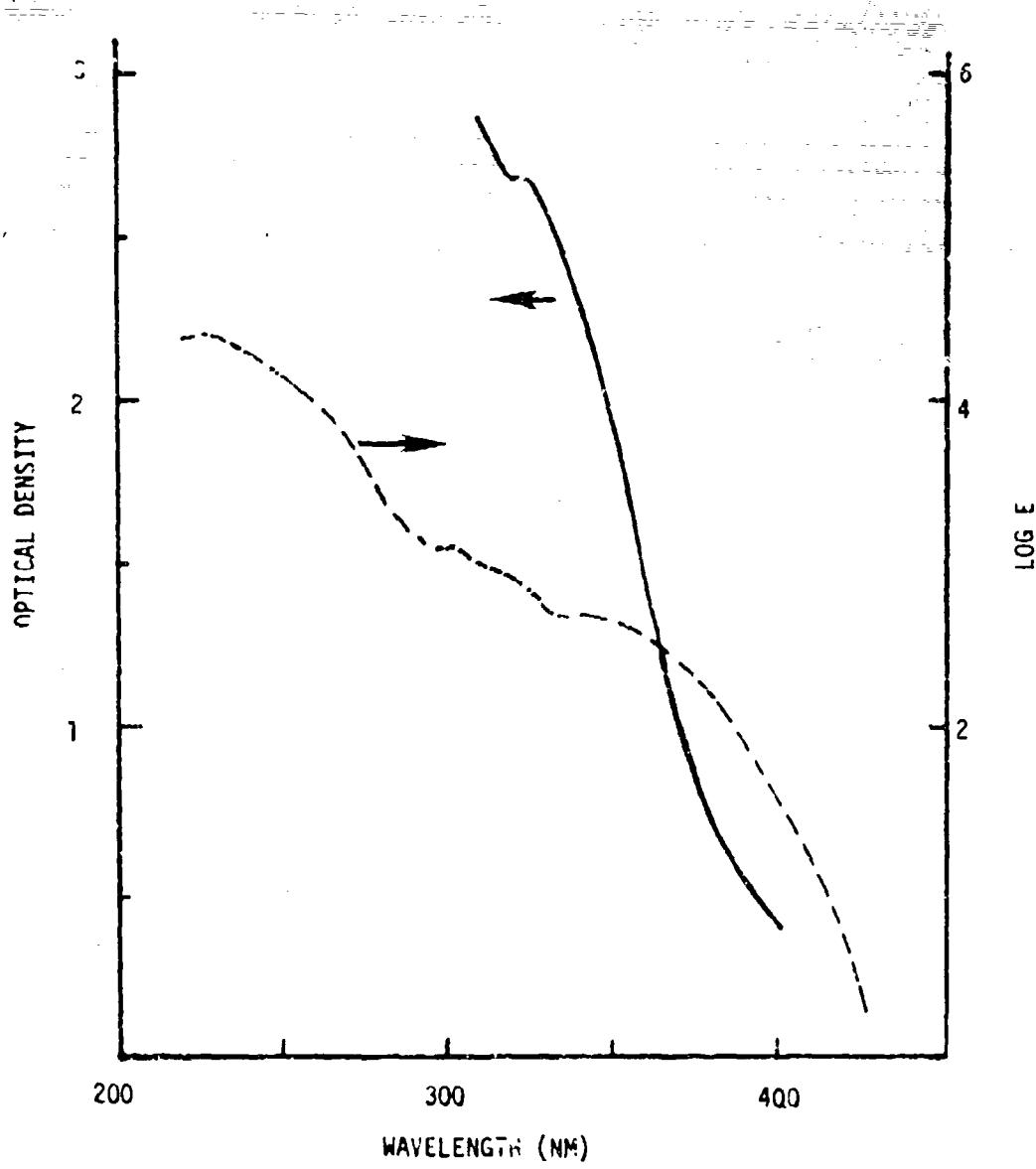


FIGURE 8 Absorption spectra of TNT crystal (—) and TNT in ethanol (---).